

ต้นฉบับ หน้าขาดหาย

3.1.2 Initiator

Benzoyl peroxide (with 25 %H₂O) from MERCK Co., Ltd. Honenbrunn, Germany. It was collected in a bottle sealed with aluminium foil to protect from the radiation from sunlight and then stored in a refrigerator at 5°C.

3.1.3 Suspending Agent

Poly(N-vinylpyrrolidone) (PVP K-90) was obtained from Chameleon Reagent, Osaka, Japan. The viscosity-average molecular weight of the polymer is 360,000.

3.1.4 Crosslinking Agent

Ethyleneglycol dimethacrylate (EGDMA) [H₂C=C(CH₃)COO CH₂]₂ was from BDH Laboratory Supplies, England.

1.1.5 Solvents

1. Acetone C₃H₆O, commercial grade: MERCK Co., Ltd. Bangkok, Thailand.
2. Isooctane (CH₃)₃ CCH₂CH(CH₃)₂, Analytical grade: Carlo Erba, Milano, Italy.
3. Toluene C₆H₅CH₃, Analytical grade: Carlo Erba, Milano, Italy.
4. Cyclohexane $\overline{\text{CH}_2(\text{CH}_2)_3\text{CH}_2}$, Analytical grade: Carlo Erba, Milano, Italy.
5. Hexane CH₃ (CH₂)₄CH₃, Analytical grade: Malinckrodt Speciality Chemicals Co. Ltd, Kentucky, U.S.A.
6. Heptane CH₃ (CH₂)₅CH₃, Analytical grade: Carlo Erba, Milano, Italy.
7. Xylene C₈H₁₀, Analytical grade: J.T. Baker, New Jersey, U.S.A..
8. Benzene C₆H₆, Analytical grade: J.T. Baker, New Jersey, U.S.A..
9. 1,2-Dichloroethylene C₂H₄Cl₂, Analytical grade: Carlo Erba, Milano, Italy.
10. Dichloromethane CH₂Cl₂, Analytical grade: Carlo Erba, Milano, Italy.
11. Chloroform CHCl₃, Analytical grade: Carlo Erba, Milano, Italy.

3.1.5 Other Chemicals

1. Aluminium oxide Al_2O_3 a chromatographic grade: Fluka, Steinheim, Switzerland.
2. Hydroquinonesulfonic acid potassium salt $(\text{OH})_2\text{C}_6\text{H}_3\text{SO}_3\text{K}$, Analytical grade: TCI, Tokyo, Japan.
3. Sodium hydroxide anhydrous pellets, NaOH , Analytical grade: Carlo Erba, Milano, Italy.
4. Sodium sulphate anhydrous (Na_2SO_4), Analytical grade: Carlo Erba, Milano, Italy.

3.2 Glassware

1. Four-necked round bottle flask 500 cm^3 .
2. Reflux condenser.
3. Thermometer.
4. Nitrogen gas tube.
5. Soxhlet apparatus.
6. Other general laboratory glasswares

3.3 Equipment

1. Scanning electron microscopy (SEM): Jeol JSM-6400, Tokyo, Japan.
2. Stereo Microscope Coupling with Luzex-F Software Program of Nireo QJ-8500: Olympus SZH 10, Japan.
3. Mechanical stirrer: Ika Werker RW 20 and EURO-ST B, Staufen, Germany.
4. Water bath: Memmert W-270, Schwabach, Germany.
5. Cooling circulator: Hakke SK55, Berlin, Germany.
6. Digital Techometer: Hioki 3403, Nagano, Japan.
7. Vacuum oven: Hotpack 273 700, P.A., U.S.A.

8. Hotplate magnetic stirrer: Snijders Scientific 334532, Tilberg, Holland.
9. Analytical balance: Precisa 300A, Switzerland.
10. Flowmeter: Koloc FK11150, Japan.
11. Differential Scanning Calorimeter: Netzsch 200, Selb/Bavaria, Germany

3.4 Polymerization Procedure

3.4.1 Seed Suspension Polymerization

Suspension polymerization reactions were carried out in a 500 cm³ round bottom flask equipped with a teflon paddle stirrer, a reflux condenser and a thermometer. The procedure used to prepare the seed polymer was as follows: The water phase composed of PVP K-90 and hydroquinonesulfonic acid potassium salt were dissolved in 100 g of water that was later introduced into the reaction flask. The aqueous phase was heated until it has reached the desired temperature, the constant agitation rate was maintained and then nitrogen gas was bubbled through the solution for deoxygenation. After 0.5 hr of nitrogen bubbling, the organic phase containing benzoyl peroxide as an initiator, which was dissolved in 10 g of the monomer mixture, composed of the monomer, crosslinking agent and diluents of toluene and isooctane, was poured into the reaction flask. The homogeneous mixture was then allowed to suspension polymerization under a constant rate of agitation and temperature. A slow stream of nitrogen gas was maintained during the polymerization. When the reaction was complete, the product was washed by distilled water and extracted by acetone in a soxhlet extractor for removing the diluents, unreacted monomer, and the residual suspending agent. Finally, the beads were dried in an oven at 60°C. Figure 3.1 shows a schematic diagram of the suspension polymerization of the crosslinked (meth)acrylate polymers.

3.4.2 Seeded Suspension Polymerization

After the seed beads of methyl acrylate and 2-ethylhexyl acrylate were cleaned, extracted and dried, they were sieved into fractions of a narrow size distribution. The sieved beads weighed 3 g were swollen in the styrene monomer solution, which was prepared with the same composition from which the seed beads were received. Swelling of the seed beads was carried out at room temperature in a closed container for 14 hr. The swollen beads were drained on a sieve to separate the excess styrene monomer and were then dispersed in a suspending medium with a constant rate of agitation. Polymerization was carried out in the same manner as that for the seed polymer.

After the polymerization was complete, the polymer beads were washed by distilled water and extracted by acetone in a soxhlet extractor. Finally, the beads were dried in the vacuum at 60°C. Figure 3.2 shows the schematic diagram of the seeded suspension polymerization of the (meth)acrylate polymers.

3.4.3 One-Stage Suspension Polymerization

The procedure of a one-stage suspension polymerization was as follows. The suspending agent (PVP K-90) was dissolved in distilled water that was then introduced into an erlenmeyer flask with a narrow neck stirred by a magnetic (stirring) bar. The aqueous phase was heated and stirred on the hot magnetic stirrer for 1.5 hr. The organic phase containing benzoyl peroxide was dissolved in 15 g of monomer mixture which was composed of (meth)acrylate monomer, styrene monomer and ethyleneglycol dimethacrylate as a crosslinker, and diluents (toluene and isooctane). An aqueous phase containing the suspending agent of PVP K-90 and the inhibitor of hydroquinonesulfonic acid potassium salt was poured into the beaker containing the organic phase. The mixture was agitated with a high-speed homogenizer. Then the homogenized mixture was polymerized in a 500 cm³ round bottom flask equipped with a teflon paddle stirrer, a reflux condenser and a thermometer. After the mixture had been heated to the desired temperature and

suspension polymerization occurred under a constant rate of agitation. A slow stream of nitrogen gas was maintained during the polymerization. When the reaction was complete, the product was washed by distilled water and extracted by acetone in a soxhlet extractor for removing the diluents, unreacted monomer and the residual suspending agent. Finally, the beads were dried in the oven at 60°C. Figure 3.3 shows the schematic diagram of one-stage suspension polymerization.

3.5 Characterization

The polymer beads were analyzed as follows.

3.5.1 Particle Size Analysis

The seed beads were brought to analysis of the particle size distribution. The wire gauze of different mesh sizes was stacked over one another varying from 2 mm. at the upper stack to 0.84 mm., 0.59 mm. and 0.42 mm. at the lower stacks, respectively. All the beads were first filled in at the top of the stack. The smaller beads will be separated from the larger ones that passed through the upper gauze to the lower gauze for further separation, whereas the larger ones will be retained on the upper wire gauze. The results of the bead size distribution were reported in weight percent.

3.5.2 Scanning Electron Microscopy (SEM)

To observe the surface, interior morphology including porosity of the beads, the beads were cut, coated and viewed conventionally by an SEM.

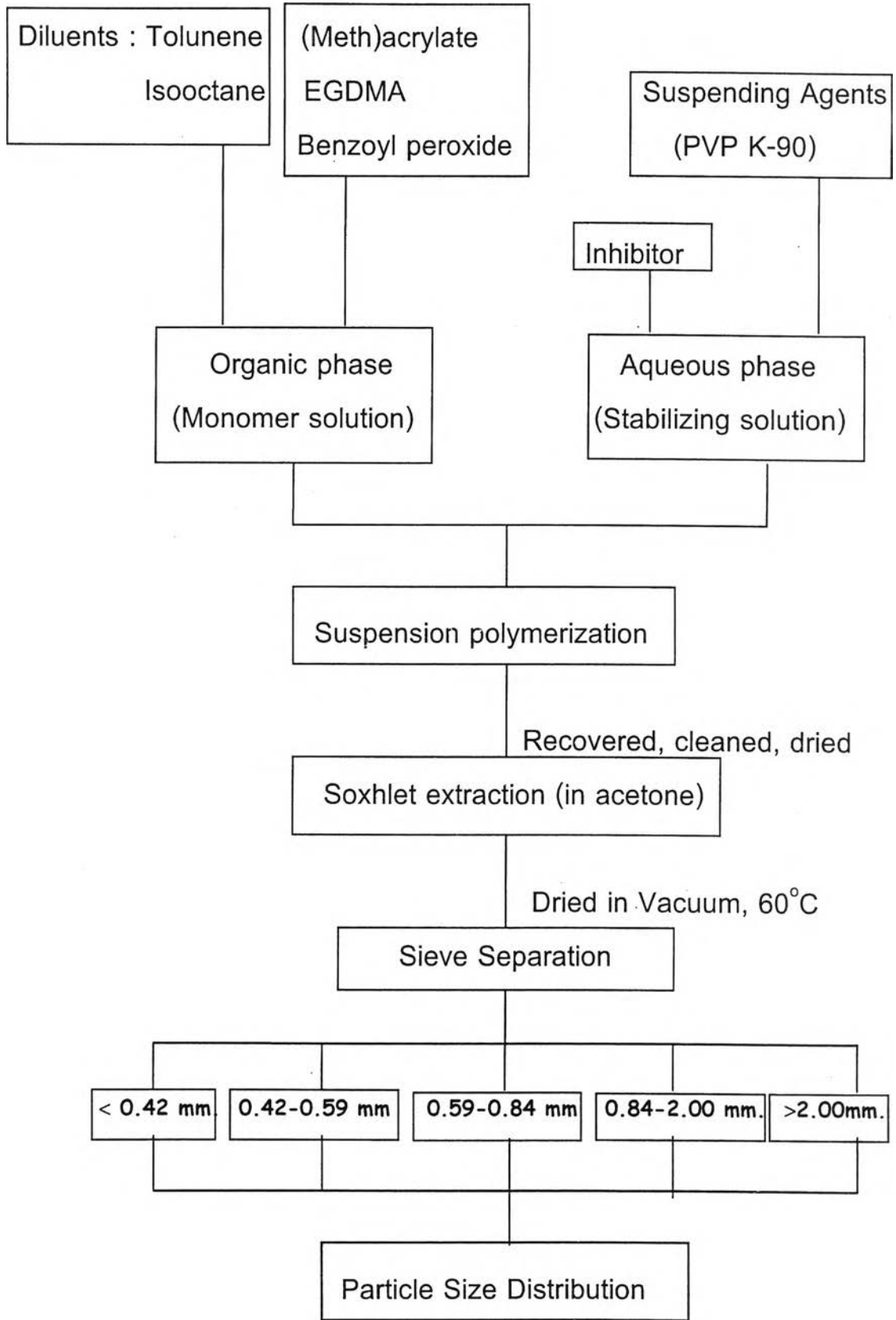
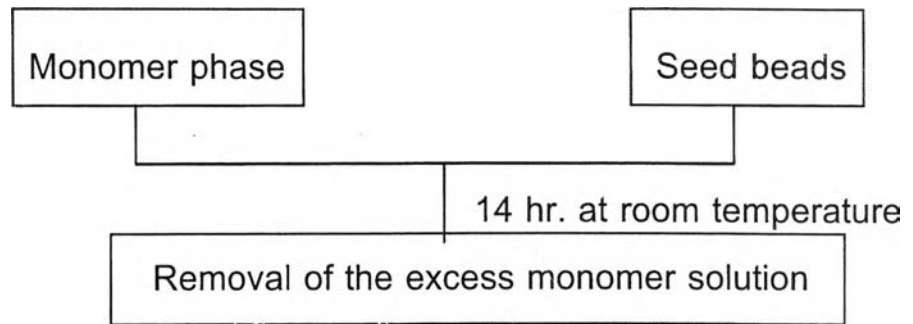


Figure 3.1 Schematic diagram of the suspension polymerization of the crosslinked (meth)acrylate polymers

-Swelling step



-Seeded suspension polymerization

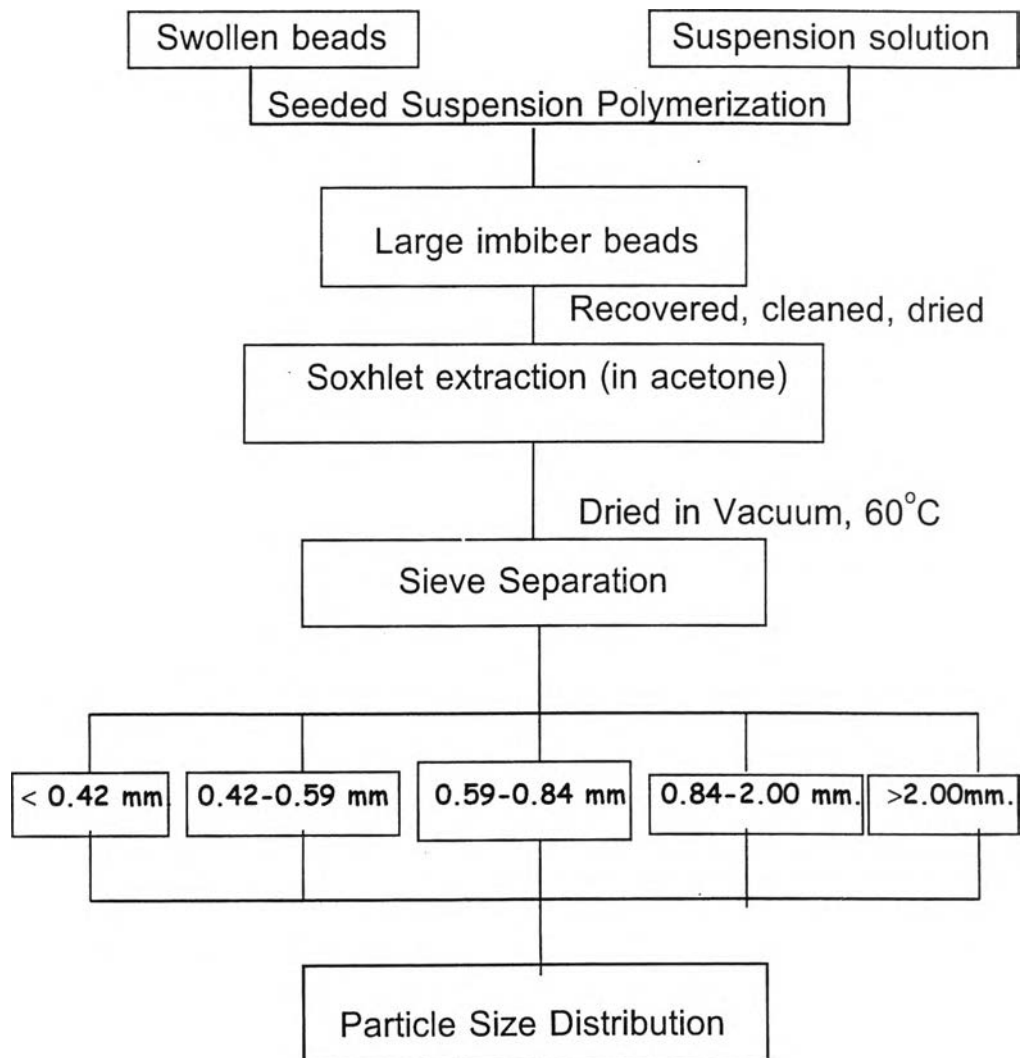


Figure 3.2 Schematic diagram of the seeded suspension polymerization

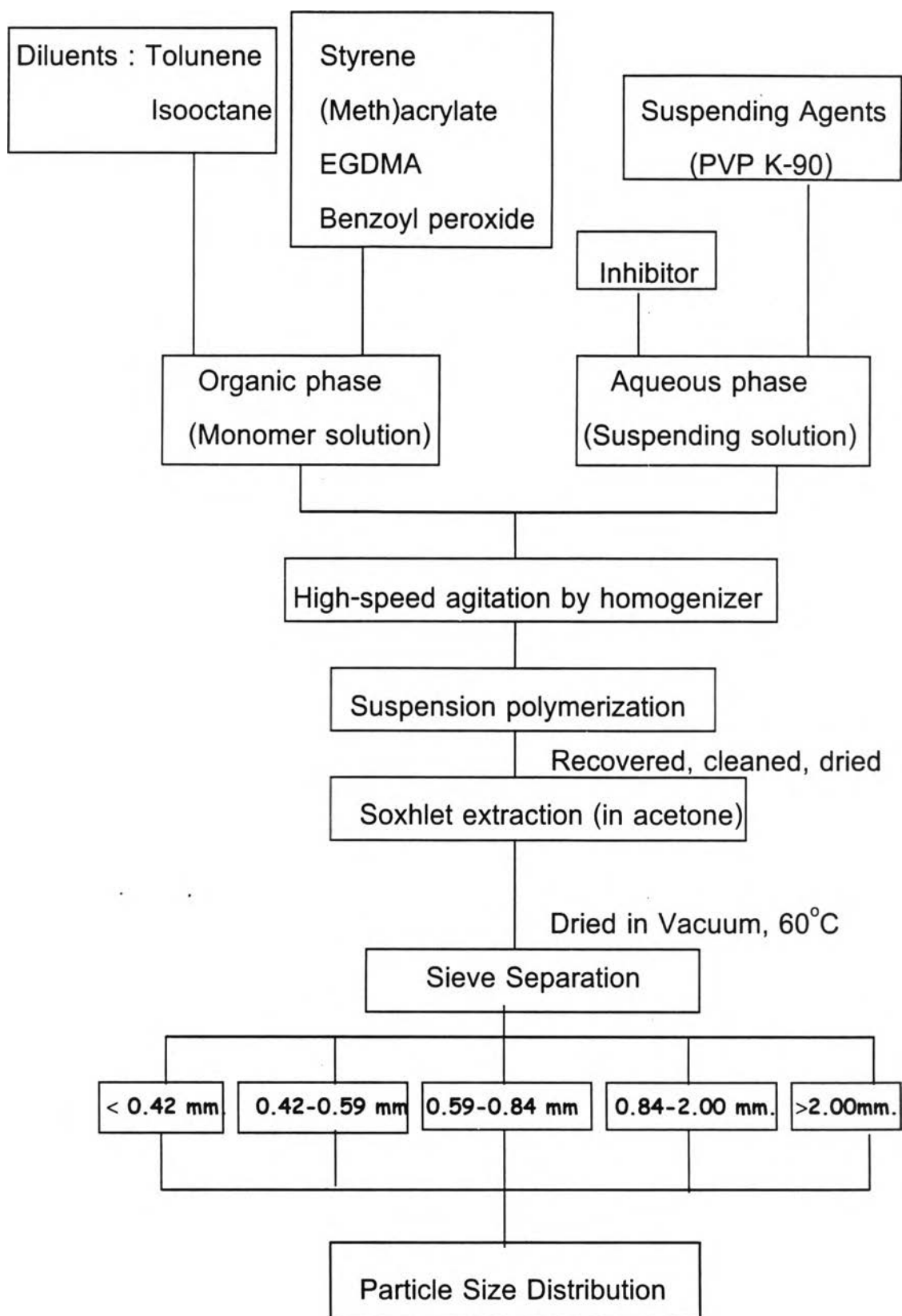


Figure 3.3 Schematic diagram of one-stage suspension polymerization

3.5.3 Swelling Properties of Beads

The swelling of the bead was determined. The dry beads were swollen in an excess amount of toluene solvent at room temperature in a test tube for 24 hr. The unused toluene was drained from the test tube. The swollen beads were weighed later.

The swelling ratio of beads was calculated by

$$S = \frac{W_s}{W_p} \quad (3-1)$$

where S is swelling ratio.

W_p is the weight of the dry beads.

W_s is the weight of the polymer beads at swelling equilibrium.

3.5.4 Determination of Thermal Properties of Beads.

Glass transition temperature of (T_g) of the polymer beads was measured using a differential scanning calorimeter. Polymer beads were weighed and put in a aluminium pan which is then covered and sealed with another pan and was put on the sensor in parallel with an empty reference pan. The polymer beads were heated at a rate of $20^\circ\text{C min}^{-1}$ and its response to heat was record.

3.5.5 Solvent Sorption and Desorption of the Imbiber Beads.

One imbiber bead was placed in a mini petri dish (1.5x1.0 cm) to immerse and swell in the excess solvent. Time zero was the time when the bead was placed into the bulk solvent and measurement of swelling kinetics was started, consequently. The bead remained in a spherical shape throughout the entire process and the variation in diameter was measured as a function of time by the stereomicroscope coupled with a Luzex-F software program. The diameter of bead could be measured by clicking three

points on the edge of the bead image on the screen. The circle around the bead image 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 in a petri dish (1.5x1.0 cm). It was covered with a lid to reduce the solvent 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.