

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1 Monomers

Styrene (Sty, C₈H₈), Shell Chemicals,

Stabilized by 10-15 ppm of tert-butylcatechol,

colorless liquid, b.p. 145-146 °C, m.p. -31 °C,

f.p. 32 °C, M = 104.15 g/mol, D = 0.906 g/cm³

Divinylbenzene (DVB, C₁₀H₁₀), Merck,

65 % DVB isomer and 33 % ethylvinylbenzene (measured by gas chromatography), stabilized by 0.2 % of 4-tert-butylpyrocatechol,

colorless liquid, b.p. 200 °C, m.p. -67 °C,

f.p. 64 °C, M = 130.19 g/mol, D = 0.919 g/cm³

Butyl Acrylate (*n*-BA, C₇H₁₂O₂), Union Carbide,

99.5 % purity stabilized by 40-60 ppm of hydroquinone,

colorless liquid, b.p. 148.8 °C, m.p. -64 °C,

f.p. 103 °C, M = 128.17 g/mol, D = 0.9015 g/cm³

2-Ethyl hexyl Acrylate (2-EHA, C₁₁H₂₀O₂), Union Carbide,

99.5 % purity stabilized by 40-60 ppm of hydroquinone,

colorless liquid, b.p. decomposes at 760 mm Hg, m.p. -90 °C,

f.p. 188 °C, M = 184.28 g/mol, D = 0.8869 g/cm³

3.1.2 Initiator

Benzoyl peroxide (BPO, $C_{14}H_{10}O_4$), Merck,

97 % purity moistened with 25 % of water,

m.p. 103-105 °C, $M = 242.23 \text{ g/mol}$

3.1.3 Suspending Agent

Poly (vinyl alcohol) (PVA), Fluka,

analytical grade, degree of polymerization 2,000,

degree of hydrolyzation 86-89 % mol, $\overline{M}_w = 100,000$

3.1.4 Solvents

Acetone (C_3H_6O), Grand Chemical Inc.,

commercial grade, colorless liquid, b.p. 56.1 °C,

$M = 58.08 \text{ g/mol}$, $D = 0.791 \text{ g/cm}^3$

Benzene (C_6H_6), J.T. Baker, analytical grade,

colorless liquid, b.p. 80.1 °C,

$M = 78.12 \text{ g/mol}$, $D = 0.879 \text{ g/cm}^3$

Carbon tetrachloride (CCl_4), J.T. Baker, analytical grade,

colorless liquid, b.p. 76.7 °C,

$M = 153.82 \text{ g/mol}$, $D = 1.594 \text{ g/cm}^3$

Chlorobenzene (C_6H_5Cl), Carlo Erba, analytical grade,

colorless liquid, b.p. 132.0 °C,

$M = 112.56 \text{ g/mol}$, $D = 1.106 \text{ g/cm}^3$

Chloroform (CHCl₃), Carlo Erba, analytical grade,

colorless liquid, b.p. 61.2 °C,

M = 119.38 g/mol, D = 1.481 g/cm³

Cyclohexane (C₆H₁₂), J.T. Baker, analytical grade,

colorless liquid, b.p. 80.7 °C,

M = 84.16 g/mol, D = 0.774 g/cm³

Cyclohexanone (C₆H₁₀O), Fluka, analytical grade,

colorless liquid, b.p. 155.6 °C,

M = 98.15 g/mol, D = 0.946 g/cm³

Ethyl acetate (C₄H₈O₂), Carlo Erba, analytical grade,

colorless liquid, b.p. 77.1 °C,

M = 88.11 g/mol, D = 0.990 g/cm³

Ethylene chloride (C₂H₄Cl₂), Carlo Erba, analytical grade,

colorless liquid, b.p. 83.0 °C,

M = 98.96 g/mol, D = 1.253 g/cm³

n-Heptane (C₇H₁₆), J.T. Baker, analytical grade,

colorless liquid, b.p. 96.0 °C,

M = 100.20 g/mol, D = 0.684 g/cm³

n-Hexadecane (C₁₆H₃₄), TCI, analytical grade,

colorless liquid, b.p. 151.0 °C,

M = 226.45 g/mol, D = 0.775 g/cm³

n-Hexane (C₆H₁₄), J.T. Baker, analytical grade,

colorless liquid, b.p. 68.7 °C,

M = 86.18 g/mol, D = 0.659 g/cm³

Methylene chloride (CH_2Cl_2), Carlo Erba, analytical grade,

colorless liquid, b.p. $39.8\text{ }^\circ\text{C}$,

$M = 84.93\text{ g/mol}$, $D = 1.325\text{ g/cm}^3$

Methyl ethyl ketone ($\text{C}_4\text{H}_8\text{O}$), Grand Chemical Inc.,

commercial grade, colorless liquid, b.p. $79.0\text{ }^\circ\text{C}$,

$M = 72.11\text{ g/mol}$, $D = 0.804\text{ g/cm}^3$

1,1,1-Trichloroethane ($\text{C}_2\text{H}_3\text{Cl}_3$), Fluka, analytical grade,

colorless liquid, b.p. $74.0\text{ }^\circ\text{C}$,

$M = 133.40\text{ g/mol}$, $D = 1.336\text{ g/cm}^3$

Trichloroethylene (C_2HCl_3), Carlo Erba, analytical grade,

colorless liquid, b.p. $87.1\text{ }^\circ\text{C}$,

$M = 131.39\text{ g/mol}$, $D = 1.463\text{ g/cm}^3$

Toluene (C_7H_8), J.T. Baker, analytical grade,

colorless liquid, b.p. $110.6\text{ }^\circ\text{C}$,

$M = 92.14\text{ g/mol}$, $D = 0.867\text{ g/cm}^3$

Xylene (C_8H_{10}), J.T. Baker, analytical grade,

colorless liquid, b.p. $138.5\text{ }^\circ\text{C}$,

$M = 106.17\text{ g/mol}$, $D = 0.864\text{ g/cm}^3$

3.1.5 Other Chemicals

Aluminum oxide (Al_2O_3), Fluka, chromatography grade,

γ -form, 100-125 mesh, $M = 101.96\text{ g/mol}$

Sodium hydroxide (NaOH), Carlo Erba, analytical grade,

$M = 40.0\text{ g/mol}$

Sodium sulfate anhydrous ($\text{Na}_2\text{SO}_4\text{.anh.}$), Carlo Erba,
analytical grade, $M = 142.04 \text{ g/mol}$

3.2 Glassware

1. 4-necked round bottom flask, $1,000 \text{ cm}^3$
2. Liebig condenser
3. Dropping funnel
4. Nitrogen gas inlet and outlet tube
5. Soxhlet apparatus
6. Thermometer
7. Other general laboratory glassware

3.3 Equipment

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| 1. Flowmeter | : Cole Parmer, U.S.A. |
| 2. Mechanical Stirrer | : Ika Werker RW20, Germany |
| 3. Stirring type | : Semicircular Teflon Paddle |
| 4. Digital Thermostat Oil Bath | : Yamato BF600, Japan |
| 5. Refrigerated Circulating Bath | : Haake SK55, Germany |
| 6. Digital Tachometer | : Digicon DT-240P, U.S.A. |
| 7. Vacuum Oven | : Hotpack 273700, U.S.A. |
| 8. Scanning Electron Microscope (SEM) | : Jeol JSM-6400, Japan |
| 9. Differential Scanning Calorimeter (DSC) | : Perkin Elmer DSC 7, U.S.A. |

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| 10. FT-IR Spectrometer | : Perkin Elmer 1760X, U.S.A. |
| 11. Heating Mantle | : Horst, Germany |
| 12. Analytical Balance | : Precisa 300A, Switzerland |
| 13. Stereo Microscope Coupling with Luzex-F Software Programme of
Nireo QJ 8500 | : Olympus SZH10, Japan |
| 14. Mercury Pore Sizer | : Micromeritic 9320, U.S.A. |

3.4 Procedures

3.4.1 Purification of Chemicals

3.4.1.1 Styrene and Other Monomers

The monomer was purified by washing with 10 % aqueous sodium hydroxide solution in a separatory funnel to remove an inhibitor. The mixture was mixed by shaking vigorously and the stopper was frequently opened to release the pressure. The organic phase and aqueous phase were left to enable complete separation and the red aqueous solution was then removed. The same procedure was repeated until the aqueous solution remained colorless. The monomer was then washed 3 times with distilled water to remove sodium hydroxide until the litmus paper did not change its original color, and was subsequently dried over sodium sulfate anhydrous. Finally, it was passed through an activated aluminum oxide column to remove the inhibitor, then stored in a dark brown bottle in a refrigerator at 0 to 4 °C prior to use (storage time should be less than two weeks).

3.4.1.2 Solvents

The commercial grade solvents were purified by fractional distillation at an atmospheric pressure prior to use, and the other solvents were used without further purification.

3.4.1.3 Other Chemicals

The other chemicals were used as received.

3.4.2 Synthesis of Styrene-divinylbenzene Copolymer

3.4.2.1 Suspension Copolymerization of Styrene and Divinylbenzene with Benzoyl peroxide

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

The solution of poly(vinyl alcohol) as suspending agent was prepared and charged into a 1,000-cm³ reaction flask which was immersed in a thermostated oil bath to maintain a constant temperature and was equipped with a variable mechanical stirrer, a thermometer, a reflux condenser, and a nitrogen gas inlet tube. The suspending agent solution was preheated at 70 °C for 20 minutes.

The monomer solution phase containing styrene monomer, divinylbenzene as a crosslinking agent, benzoyl peroxide as an initiator and organic solvents was added into the reaction flask in which the suspending agent solution was stirred at an agitation speed of 270 rpm. The reaction was allowed to proceed for 10 hours under nitrogen atmosphere. After polymerization, the copolymer beads were washed with

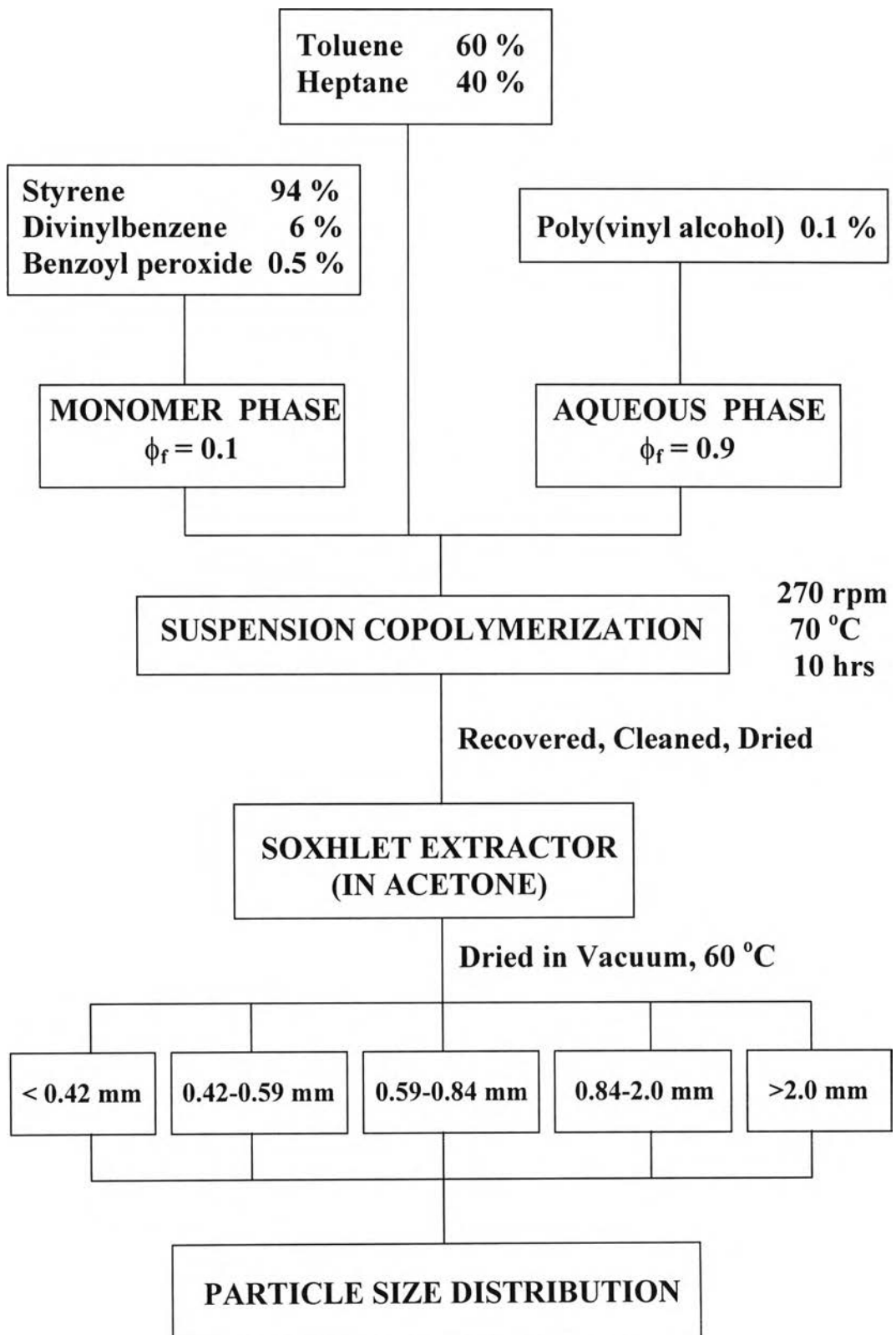


Figure 3.1 Rough diagram of suspension copolymerization of styrene-divinylbenzene copolymer beads.

water and extracted with acetone in a soxhlet extractor for 10 hours to remove the diluents, unreacted monomer and residual suspending agent. Subsequently, beads were dried in a vacuum oven at 60 °C for 24 hours.

3.4.2.2 The Effect of Monomer Phase Weight Fraction

Suspension copolymerization of styrene and divinylbenzene was repeated using the monomer phase weight fraction given in Table 3.1.

Table 3.1 Various monomer phase weight fractions for suspension copolymerization of styrene and divinylbenzene*

Runs	Monomer Phase Weight Fraction
M06	0.06
M08	0.08
M10	0.10
M17	0.17

* Polymerizations are carried out at 6 % DVB, 0.5 % BPO, 0.1 % PVA, 70 °C, 10 hours, 270 rpm, Tol/Hep = 100/0.

3.4.2.3 The Effect of Agitation Rate

Suspension copolymerization of styrene and divinylbenzene was repeated using agitation rates given in Table 3.2.

Table 3.2 Various agitation rates for suspension copolymerization of styrene and divinylbenzene*

Runs	Agitation Rate (rpm)
R20	200
R27	270
R30	300

* Polymerizations are carried out at 6 % DVB, 0.5 % BPO, 0.1 % PVA, 70 °C, 10 hours, Tol/Hep = 100/0, Monomer phase weight fraction = 0.1.

3.4.2.4 The Effect of the Reaction Temperature

Suspension copolymerization of styrene and divinylbenzene was repeated using reaction temperatures given in Table 3.3.

Table 3.3 Various reaction temperatures for suspension copolymerization of styrene and divinylbenzene*

Runs	Reaction Temperature (°C)
T60	60
T70	70
T80	80

* Polymerizations are carried out at 6 % DVB, 0.5 % BPO, 0.1 % PVA, 10 hours, 270 rpm, Monomer phase weight fraction = 0.1, Tol/Hep = 100/0.

3.4.2.5 The Effect of Reaction Time

Suspension copolymerization of styrene and divinylbenzene was repeated using reaction times given in Table 3.4.

Table 3.4 Various reaction times for suspension copolymerization of styrene and divinylbenzene*

Runs	Reaction Times (hours)
t06	6
t08	8
t10	10
t15	15

* Polymerizations are carried out at 6 % DVB, 0.5 % BPO, 0.1 % PVA, 70 °C, 270 rpm, Monomer phase weight fraction = 0.1, Tol/Hep = 100/0.

3.4.2.6 The Effect of Initiator Concentration

Suspension copolymerization of styrene and divinylbenzene was repeated using initiator concentrations given in Table 3.5.

Table 3.5 Various initiator concentrations for suspension copolymerization of styrene and divinylbenzene*

Runs	Initiator Concentration (% wt based on monomer phase)
I01	0.1
I05	0.5
I10	1.0
I20	2.0

* Polymerizations are carried out at 6 % DVB, 0.1 % PVA, 70 °C, 10 hours, 270 rpm, Monomer phase weight fraction = 0.1, Tol/Hep = 100/0.

3.4.2.7 The Effect of Crosslinking Agent Concentration

Suspension copolymerization of styrene and divinylbenzene was repeated using crosslinking agent concentrations given in Table 3.6.

Table 3.6 Various crosslinking agent concentrations for suspension copolymerization of styrene and divinylbenzene *

Runs	Crosslinking Agent Concentration (% wt based on monomer phase)
D03	3
D06	6
D09	9
D12	12
D15	15

* Polymerizations are carried out at 0.5 % BPO, 0.1 % PVA, 70 °C, 10 hours, 270 rpm, Monomer phase weight fraction = 0.1, Tol/Hep = 100/0.

3.4.2.8 The Effect of Suspending Agent Concentration

Suspension copolymerization of styrene and divinylbenzene was repeated using suspending agent concentrations given in Table 3.7.

Table 3.7 Various suspending agent concentrations for suspension copolymerization of styrene and divinylbenzene*

Runs	Suspending Agent Concentration (% wt based on monomer phase)
P05	0.05
P10	0.10
P15	0.15
P20	0.20

* Polymerizations are carried out at 6 % DVB, 0.5 % BPO, 70 °C, 10 hours, 270 rpm, Monomer phase weight fraction = 0.1, Tol/Hep = 100/0.

3.4.2.9 The Effect of Diluent Composition

Suspension copolymerization of styrene and divinylbenzene was repeated using diluent compositions given in Table 3.8.

Table 3.8 Various diluent compositions for suspension copolymerization of styrene and divinylbenzene*

Runs	Toluene/Heptane (% wt based on monomer phase)
H00	100/0
H02	80/20
H04	60/40
H06	40/60
H08	20/80

* Polymerizations are carried out at 6 % DVB, 0.5 % BPO, 0.1 % PVA, 70 °C, 10 hours, 270 rpm, Monomer phase weight fraction = 0.1.

3.4.2.10 The Effect of Monomer Composition

Suspension copolymerization of styrene and divinylbenzene was repeated using monomer composition given in Table 3.9.

Table 3.9 Various monomer compositions for suspension copolymerization of styrene and divinylbenzene*

Runs	Monomer Composition (% wt based on monomer phase)			
	Sty	DVB	<i>n</i> -BA	2-EHA
B24	70	6	24	-
B47	47	6	47	-
E24	70	6	-	24
E47	47	6	-	47

* Polymerizations are carried out at 0.5 % BPO, 0.1 % PVA, 70 °C, 10 hours, 270 rpm, Monomer phase weight fraction = 0.1, Tol/Hep = 60/40.

3.4.3 Copolymer Characterization

3.4.3.1 Determination of Particle Size and Size Distribution of Styrene-divinylbenzene Copolymer Beads (Sieve Analysis)

The copolymer beads were brought to the 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 copolymer beads were first filled in at the top of the stack. The smaller beads were separated from the larger ones that passed through the upper gauze to the lower gauzes for further separation, whereas the larger ones had been

retained on the upper wire gauze. The results of the bead size distribution were reported in percent weight.

3.4.3.2 Determination of Swelling Properties of Styrene-divinylbenzene Copolymer Beads

The swelling measurements of the copolymer beads were carried out in toluene at room temperature. The swelling ratio, S , was determined gravimetrically by subsequent immersing the dry copolymer beads in toluene for 24 hours. The swelling ratio of the beads was calculated by

$$S = 1 + \left(\frac{W_s}{W_p} - 1 \right) \frac{\rho_p}{\rho_s} \quad (3.1)$$

where W_p is the weight of the copolymer before swelling or dry polymer weight

W_s is the weight of the copolymer at equilibrium

ρ_s and ρ_p are the densities of solvent and polymer, respectively

3.4.3.3 Determination of Crosslinking Density of Styrene-divinylbenzene Copolymer Beads

The crosslinking densities of copolymer beads were determined using the Flory-Rehner theory. To obtain this, volume fraction (ϕ_p) of the beads is first calculated by

$$\phi_p = \frac{V_p}{V_s + V_p} \quad (3.2)$$

where V_s and V_p are the molar volume of solvent and polymer, respectively.

For polystyrene system, the polymer-solvent interaction parameter was estimated using the following formula [14]:

$$\chi_{12} = 0.431 - 0.311\phi_p - 0.036\phi_p^2 \quad (3.3)$$

One of the most important structural parameters characterizing crosslinking density is \overline{M}_c , the average molecular weight between crosslinking network. According to the theory of Flory and Rehner.

$$\overline{M}_c = -V_s \rho_p \frac{(\phi_p^{1/3} - \phi_p/2)}{[\ln(1-\phi) + \phi_p + \chi_1 \phi_p^2]} \quad (3.4)$$

Here the crosslinking density, q , is defined as the mole fraction of the crosslinking units:

$$q = \frac{M_0}{\overline{M}_c} \quad (3.5)$$

where M_0 is the molecular weight of the repeating of the copolymer.

3.4.3.4 Determination of Surface Morphology of Styrene-divinylbenzene Copolymer Beads (Scanning Electron Microscopy)

The dry copolymer beads were coated with a thin layer of gold in vacuum and photographed using scanning electron microscopy on the Joel JSM-6400 to characterize surface morphology of the copolymer beads.

3.4.3.5 Determination of Thermal Properties of Styrene-divinylbenzene Copolymer Beads

The samples were prepared by drying at 60 °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.

3.4.3.6 Determination of Styrene-divinylbenzene Copolymer Beads Density

The determination of the density of copolymer beads using the displacement technique following the ASTM D792 test method. The principle of this measurement was described in Appendix A.

3.4.3.7 Determination of Solvent Absorption and Desorption Kinetics of Styrene-divinylbenzene Copolymer Beads

One dry bead was placed in a mini petri dish (1.5 × 5 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 function of time by the stereomicroscope coupling with a Luzex-F software program. The diameter of bead could be measured by clicking three points on the edge of the copolymer bead on the monitor screen. The circle around the bead

and the diameter were shown. The accuracy of the bead diameter measured by this method was 0.00001 mm.

For desorption kinetics measurements, a fully swollen bead was placed on a piece of filter paper substrate (38.5 cm^3) in a petri dish ($1.5 \times 10 \text{ cm}$). It was covered to reduce evaporation and keep out 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.

3.4.3.8 Determination of Pore Properties of Styrene-divinylbenzene Copolymer Beads

The determination of surface area, pore volume used the mercury porosimetry technique. The principle of this measurement was described in Appendix B.