CHAPTER III

EXPERIMENTAL

3.1 Chemical

3.1.1 Monomers

Methyl Methacrylate (MMA), supported by
Siam Chemical Co., Ltd.
$C_5H_8O_2$, MW = 100 g/mol

Butyl Methacrylate (BMA), Fluke,
GC grade, $C_8H_{14}O_2$, MW = 142.20 g/mol,
b.p. 162-165°C, Density = 0.895 g/cm^3

Lauryl Methacrylate (LMA), Fluka,
GC grade, $C_{16}H_{30}O_2$, MW = 254.42 g/mol,
b.p. 142°C, Density = 0.873 g/cm^3

Dodecyl Acrylate (DA), Fluka,
GC grade, $C_{15}H_{28}O_2$, MW = 240.39 g/mol,
Density = 0.875 g/cm^3

Stearyl Acrylate (SA), Fluka,
GC grade, $C_{21}H_{40}O_2$, MW = 324 g/mol,
Density = 0.8 g/cm^3

3.1.2 Crosslinking agent

Divinylbenzene ($C_{10}H_{10}$), Merck-Schuchardt,
Synthesis grade, stabilized with 0.2% 4-*tert*-butylpyrocatechol,
colorless liquid, MW = 130.19 g/mol

3.1.3 Initiator

Benzoyl peroxide (BPO), Ajax chemicals,

$C_{14}H_{10}O_4$, Organic peroxides, type C, solids,

Moistened with 25% water, Assay 75% max,

MW = 242.23 g/mol

3.1.4 Suspension Agent

Poly(vinyl alcohol) (PVA), Fluka,

Analytical grade, degree of polymerization 2,000,

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

3.1.5 Solvents

Acetone (C_3H_6O), Grand Chemical Inc.,

commercial grade, colorless liquid, b.p. 56.1 ^{o}C,

MW = 58.08 g/mol, Density = 0.791 g/cm^3

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

colorless liquid, b.p. 80.1 ºC,

MW = 78.12 g/mol, Density = 0.879 g/cm^3

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

colorless liquid, b.p. 76.7 ºC,

MW = 153.82 g/mol, Density = 1.594 g/cm^3

Chlorobenzene (C_6H_5Cl), Carlo Erba, analytical grade,

colorless liquid, b.p. 76.7 ºC,

MW = 112.56 g/mol, Density = 1.106 g/cm^3

Chloroform (CH_3Cl), Carlo Erba, analytical grade,

colorless liquid, b.p. 61.2 ºC,

MW = 119.38 g/mol, Density = 1.481 g/cm^3

Cyclohexane (C_6H_{12}), J.T.Baker, analytical grade,

colorless liquid, b.p. 80.7 ºC,

MW = 84.16 g/mol, Density = 0.774 g/cm^3

Cyclohexanone (C_6H_5O), Fluka, analytical grade,

colorless liquid, b.p. 155.6°C,

MW = 98.15 g/mol, Density = 0.946 g/cm^3

Ethylene chloride ($C_2H_4Cl_2$), Carlo Erba, analytical grade,

colorless liquid, b.p. 83.0°C,

MW = 98.96 g/mol, Density = 1.253 g/cm^3

n-**Heptane** (C_7H_{16}), J.T. Baker, analytical grade,

colorless liquid, b.p. 96.0 °C,

MW = 100.20 g/mol, Density = 0.684 g/cm^3

n-**Hexane** (C_6H_{14}), J.T.Baker, analytical grade,

colorless liquid, b.p. 68.7°C,

MW = 86.18 g/mol, Density = 0.659 g/cm^3

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

colorless liquid, b.p. 39.8°C,

MW = 84.93 g/mol, Density = 1.325 g/cm^3

Trichloroethylene (C_2HCl_3), Carlo Erba, analytical grade,

colorless liquid, b.p. 87.1°C,

MW = 131.39 g/mol, Density = 1.463 g/cm^3

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

colorless liquid, b.p. 110.6 °C,

MW = 92.14 g/mol, Density = 0.867 g/cm^3

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

colorless liquid, b.p. 138.5°C,

MW = 106.17 g/mol, Density = 0.864 g/cm^3

n-**Amyl alcohol** ($C_5H_{12}O$), analytical Carlo Erba,

Reagent grade, colorless liquid,

Density = 0.817 g/cm^3

3.1.6 Other Chemicals

Aluminum oxide (Al_2O_3), Fluka, chromatography grade,

γ-form, 100-125 mesh, MW = 101.96 g/mol

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

MW = 40.0 g/mol

Sodium sulfate anhydrous (Na_2SO_4.anh.), Carlo Erba,

Analytical grade, MW = 142.04 g/mol

3.2 Glassware

1. 4-necked round bottom flask, 1,000 cm^3
2. Liebig condenser
3. Nitrogen gas inlet and outlet tube
4. Soxhlet apparatus
5. Thermometer
6. Other general laboratory glassware

3.3 Equipment

1. Flowmeter	: Cole Parmer, U.S.A.
2. Mechanical stirrer	: Ika Werker RW20, Germany
3. Digital Thermostat Oil Bath	: Yamato BF600, Japan
4. Refrigerated Circulating Bath	: Haaka SK55, Japan
5. Digital Tachometer	: Digicon DT-240P, U.S.A.
6. Vacuum Oven	: Hotpack 273700, U.S.A.
7. Scanning Electron Microscope (SEM)	: Jeol JSM-6400, Japan
8. FT-IR Spectrometer	: Nicolet, USA
9. Heating Mantle	: Horst, Germany
10. Analytical Balance	: Precise 300A, Switzerland
11. Stereo Microscope Coupling with Luzer-F Software Program of Nireo QJ8500	: Olympus SZH10, Japan

3.4 Procedures
3.4.1 Purification of chemicals
3.4.1.1 Monomers

Methyl methacrylate (MMA), butyl methacrylate (BMA), lauryl methacrylate (LMA), dodecyl acrylate (DA) and stearyl acrylate (SA) were used as a monomer in

each polymerization. Each monomer was washed with 10 % aqueous sodium hydroxide solution in a separatory funnel in order to remove the inhibitor. The mixture was mixed thoroughly 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 more with distilled water to remove the remaining hydroxyl ion until the litmus paper did not change its original color. Then, it was dried over anhydrous sodium sulfate. Finally, it was passed through an activated aluminum oxide column to remove the residual 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). Stearyl acrylate which is in the solid state at room temperature was used without further purification.

3.4.1.2 Solvents

The commercial grade solvents were purified by fractional distillation at 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 copolymers

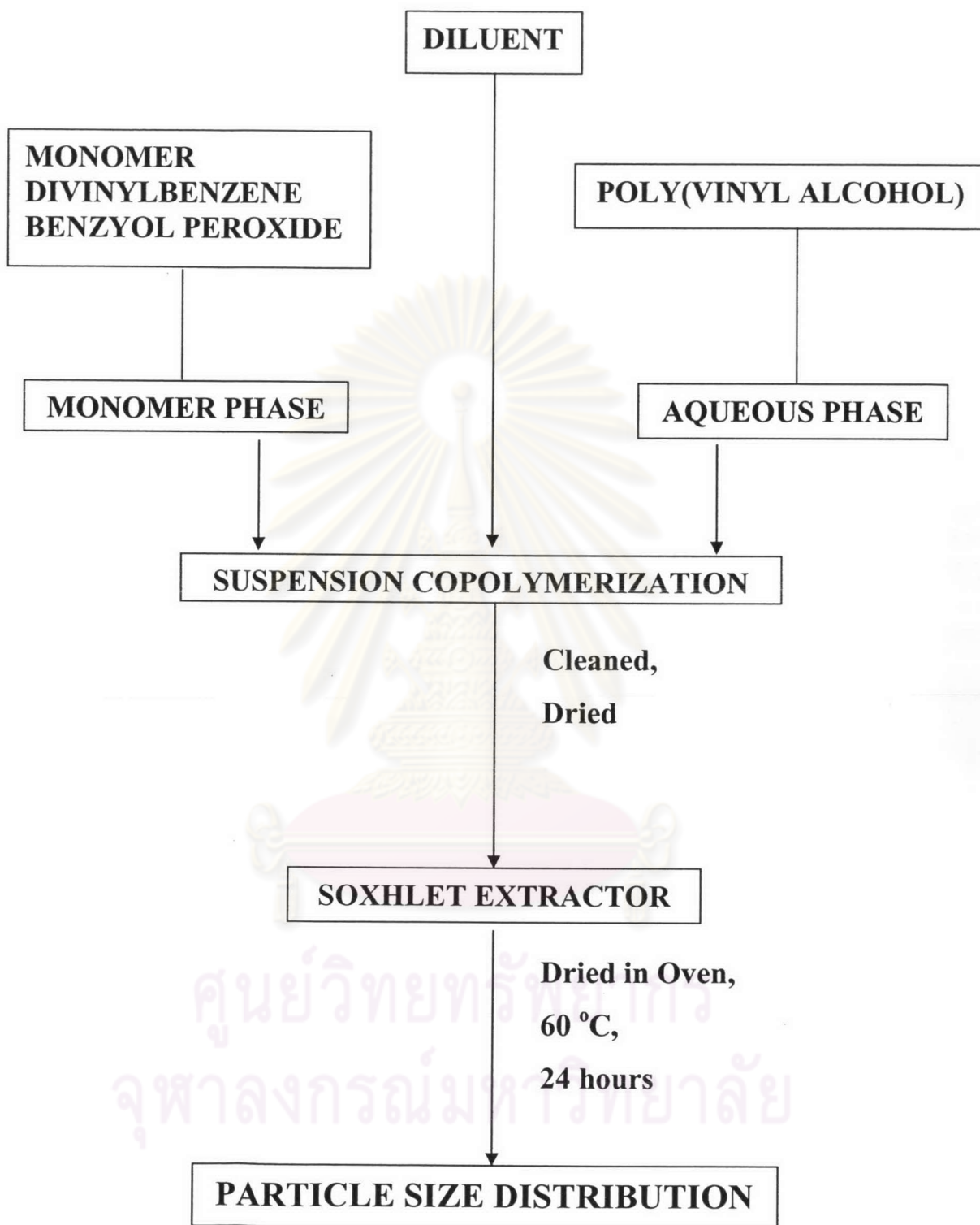### 3.4.2.1 Suspension copolymerization of methyl methacrylate and divinylbenzene

The methyl methacrylate-divinylbenzene copolymer was prepared by suspension polymerization using a free-radical mechanism. The procedure of suspension copolymerization of methyl methacrylate-divinylbenzene beads was summarized as shown in Figure 3.1.

The solution of poly(vinyl alcohol), as a suspension stabilizer, was prepared and poured into a 1-L, 4-necked round bottom flask reactor which was immersed in a thermostat oil bath to maintain a constant temperature. It was equipped with a variable mechanical stirrer, a thermometer, a reflex condenser and a nitrogen gas inlet tube as shown in Figure 3.2. The suspending agent solution was preheated at 70 ^{o}C for 20 minutes.

The monomer solution phase containing methyl methacrylate monomer, divinylbenzene crosslinking agent, benzoyl peroxide initiator and toluene as an organic solvent first mixed well before adding to the reaction flask, which contained the suspending agent solution, was stirred at an agitation speed of 140 rpm. The reaction was allowed to continue for 5 h at 70 ^{o}C under nitrogen atmosphere. At the end of the polymerization, the copolymer beads were obtained and washed with distillation water for many times. Then the copolymer beads were dried in an oven at 60°C for 24 h. The dried copolymer beads were extracted with acetone in Soxhlet extractor for 24 h to remove the diluent, residual suspending agent and unreacted monomer. Subsequently, the copolymer beads were dried in the oven at 60°C for 24 h. The polymer sample was dried again in vacuum oven at room temperature for 24 h for any characterization.

3.4.2.2   The effect of the monomer type

Suspension copolymerization was varied with monomer type from butyl methacrylate, lauryl methacrylate, dodecyl acrylate to stearyl acrylate. The copolymer beads of any monomers were produced by the same suspension polymerization method described in previous part, whereas the reaction was allowed to continue for 20 h at 70 ^{o}C. The copolymer beads were extracted with tetrahydrofuran (THF) in Soxhlet extractor for 24 h to remove residue chemicals and impurities.

Figure 3.1 Diagram of suspension copolymerization of various monomers and divinylbenzene crosslinking agent.

3.4.2.3 The effect of crosslinking agent concentration

Suspension copolymerization of various monomers and divinylbenzene was varied with crosslinking agent concentration as shown in Table 3.1.

Table 3.1 Crosslinking agent concentrations for suspension copolymerization of any monomer and divinylbenzene

Monomer	Runs	Crosslinking agent concentration (% wt based on monomer phase)
Methyl methacrylate	MMA000	0
(MMA)	MMA025	0.025
	MMA050	0.500
	MMA100	1.000
	MMA150	1.500
Butyl methacrylate	BA000	0
(BMA)	BA030	0.030
	BA050	0.050
	BA100	1.000
	BA200	2.000
Lauryl methacrylate	LMA000	0
(LMA)	LMA010	0.100
	LMA030	0.300
	LMA050	0.500
	LMA100	1.000
	LMA200	2.000
Dodecyl acrylate	DA000	0
(DA)	DA050	0.500
	DA100	1.000
	DA150	1.500
	DA200	2.000

Monomer	Runs	Crosslinking agent concentration (% wt based on monomer phase)
Stearyl acrylate (SA)	SA000	0
	SA050	0.500
	SA100	1.000
	SA150	1.500
	SA200	2.000

Polymerization was carried out with 0.5% BPO, 0.2% PVA at 70°C for 5 h for methyl methacrylate and 20 h for other monomers, 140 rpm when the monomer phase weight fraction is 0.14 and 100% toluene as a solvent.

3.4.2.4 The effect of diluent composition

Suspension copolymerization of methyl methacrylate and divinylbenzene was varied with n-heptane as a nonsolvent in the diluent composition. The copolymerization of butyl methacrylate and divinylbenzene was varied with n-amyl alcohol as a nonsolvent in the diluent composition as shown in Table 3.2.

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Table 3.2 Various diluent compositions for suspension copolymerization of methyl methacrylate and divinylbenzene and butyl methacrylate and divinylbenzene

Monomers	Runs	Diluent composition (% wt based on monomer phase)
Methyl methacrylate (MMA)	H00	0
	H20	20
	H40	40
	H60	60
	H80	80
Butyl methacrylate (BMA)	A00	0
	A20	20
	A40	40
	A60	60
	A80	80

Copolymerization of MMA and DVB was carried out at 0.5% BPO, 0.2% PVA, 1% DVB, 70°C, 5 hours, 140 rpm, monomer phase weight fraction is 0.14. Copolymerization of BMA and DVB was carried out at 0.5% BPO, 0.2% PVA, 0.5% DVB, 70°C, 20 hours, 140 rpm, monomer phase weight fraction is 0.14.

3.4.2.5 The effect of monomer phase weight fraction

Suspension copolymerization of methyl methacrylate and divinylbenzene was varied with the monomer phase weight fraction as shown in Table 3.3.

Table 3.3 Various monomer phase weight fractions for suspension copolymerization of methyl methacrylate and divinylbenzene

Runs	Monomer phase weight fraction
M10	0.10
M12	0.12
M14	0.14
M16	0.16

Polymerization was carried out at 0.5% BPO, 0.2% PVA, 1% DVB, $70^{o}C$, 5 h, 140 rpm and 100% toluene.

3.4.2.6   The effect of agitation rate

Suspension copolymerization of methyl methacrylate and divinylbenzene was varied with agitation rates as shown in Table 3.4.

Table 3.4 Various agitation rates for suspension copolymerization of methyl methacrylate and divinylbenzene

Runs	agitation rate (rpm)
R12	120
R13	130
R14	140
R15	150

Polymerization was carried out at 0.5% BPO, 0.2% PVA, 1% DVB, $70^{o}C$, 5 hours, monomer phase weight fraction is 0.14 and 100% toluene.

3.4.2.7 The effect of the reaction temperature

Suspension copolymerization of methyl methacrylate and divinylbenzene was varied with reaction temperature as shown in Table 3.5.

Table 3.5 Various reaction temperatures for suspension copolymerization of methyl methacrylate and divinylbenzene

Runs	Reaction Temperature (^{o}C)
T60	60
T70	70
T80	80

Polymerization was carried out at 0.5% BPO, 0.2% PVA, 1% DVB, 5 hours, 140 rpm, with a monomer phase weight fraction of 0.14 in 100% toluene.

3.4.2.8 The effect of the reaction time

Suspension copolymerization of methyl methacrylate and divinylbenzene was varied with reaction time as shown in Table 3.5.

Table 3.6 Various reaction times for suspension copolymerization of methyl methacrylate and divinylbenzene

Runs	Reaction Time (hours)
t35	3.5
t50	5.0
t65	6.5
t80	8.0

Polymerization was carried out at 0.5% BPO, 0.2% PVA, 1% DVB, 70°C, 140 rpm, with a monomer phase weight fraction of 0.14 in 100% toluene.

3.4.2.9 The effect of initiator concentration

Suspension copolymerization of methyl methacrylate and divinylbenzene was varied with initiator concentrations as shown in Table 3.7.

Table 3.7 Various initiator concentrations for suspension copolymerization of methyl methacrylate and divinylbenzene

Runs	Initiator Concentration (% wt based on monomer phase)
I012	0.125
I025	0.250
I050	0.500
I100	1.000

Polymerization was carried out at 0.2% PVA, 1% DVB, 70°C, 140 rpm, 5 h with a monomer phase weight fraction of 0.14 in 100% toluene.

3.4.2.10 The effect of suspending agent concentration

Suspension copolymerization of methyl methacrylate and divinylbenzene was varied with suspending agent concentrations as shown in Table 3.8.

Table 3.8 Various suspending agent concentrations for suspension copolymerization of methyl methacrylate and divinylbenzene

Runs	Suspending Agent Concentration (% wt based on monomer phase)
S10	0.10
S15	0.15
S20	0.20
S25	0.25

Polymerization was carried out at 0.5% BPO, 1% DVB, 70°C, 140 rpm, 5 h, monomer phase weight fraction of 0.14 in 100% toluene.

3.4.2.11 The effect of comonomer type

Suspension copolymerization of methyl methacrylate and divinylbenzene was varied with comonomer types as shown in Table 3.9.

Table 3.9 Various comonomer types for suspension copolymerization of methacrylate and divinylbenzene

Runs	Comonomer
MMA-BMA	Butyl methacrylate
MMA-LMA	Lauryl methacrylate
MMA-DA	Dodecyl acrylate
MMA-SA	Stearyl acrylate

Polymerization was carried out at 0.5% BPO, 0.5% DVB, 0.2% PVA, 70°C, 140 rpm, 20 h with a monomer phase weight fraction of 0.14, MMA/comonomer ratio = 4:1 in 100% toluene.

3.4.3 Copolymer Characterization

3.4.3.1 Determination of particle size and size distribution of methacrylate-divinylbenzene copolymer beads (Sieve Analysis)

The copolymer beads were brought to the analysis of particle size distribution. The 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 gauze 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 methyl methacrylate-divinylbenzene copolymer beads

The swelling measurements of the copolymer beads were carried out in toluene or lube oil at room temperature. To determine the swelling ratio, S, by immersing the dry copolymer beads in toluene for one week until reaching equilibrium. The swelling ratio of the copolymer beads was calculated by

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

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

3.4.3.3 Determination of crosslinking density of methyl methacrylate-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

$$\phi_p = \frac{V_p}{V_s + V_p} \tag{3.2}$$

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

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.

$$\overline{M_c} = -V_s \rho_p \frac{\left(\phi_p^{1/3} - \dfrac{\phi_p}{2}\right)}{\left[\ln(1-\phi) + \phi_p + \chi_1 \phi_p^2\right]} \tag{3.3}$$

The polymer-solvent interaction parameter for PMMA/toluene is 0.53 ± 0.04

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

$$q = \frac{M_o}{M_c} \tag{3.4}$$

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

3.4.3.4 Determination of surface morphology of methyl methacrylate-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 density of methyl methacrylate-divinylbenzene copolymer beads density

The determination of the density of copolymer beads using the displacement technique following the ASTM D792 test method was carried out of this measurement.

3.4.3.6 Determination of solvent absorption kinetics of methyl-methacrylate 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. The bead remained spherical throughout the entire process and the variation in diameter was measured as a function of time by Olympus 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.

3.4.3.7 Determination of solubility parameter of methyl-methacrylate-Divinylbenzene-Alkyl(meth)acrylate terpolymer beads

The swelling measurements of the terpolymer beads were carried out in several solvents with known solubility parameter at room temperature. To determine the swelling ratio, S, by immersing the dry copolymer beads in each solvent for one

week until reaching equilibrium. The swelling ratio of the copolymer beads was calculated by

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

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

The swelling ratio reaches a maximum when the solubility parameter of the solvent nearly matches that of the copolymer.