CHAPTER 3

EXPERIMENTAL

3.1 Materials, apparatus, and analytical instruments

3.1.1 Materials

3.1.1.1 Monomers

Styrene (St), MW = 104.0

$C_6H_5CH=CH_2$

Commercial grade

Kishida Chemical Co., Ltd.

Methyl methacrylate (MMA), MW = 100.12

$CH_2=CCH_3COOCH_3$

Commercial grade

Kishida Chemical Co., Ltd.

n-Butyl methacrylate (n-BMA), MW = 142.2

$CH_2=CCH_3COO(CH_2)_3CH_3$

Commercial grade

Kishida Chemical Co., Ltd.

2-Ethylhexyl methacrylate (2-EHMA), MW = 198.31

$CH_2=CCH_3COOCH_2CH(CH_2CH_3)(CH_2)_3CH_3$

Commercial grade

Kishida Chemical Co., Ltd.

Ethyleneglycol dimethacrylate (EGDMA), MW = 198.22

$CH_2=C(CH_3)COOCH_2CH_2COOC(CH_3)=CH_2$

Commercial grade

Kishida Chemical Co., Ltd.

Divinylbenzene (DVB), MW = 130; 55% isomeric DVB and 5% saturated hydrocarbon
CH_2=CH(C_6H_4)CH:CH_2
Commercial grade
Kishida Chemical Co., Ltd.

3.1.1.2 Initiator

Benzoyl peroxide (BPO) with 25 wt% moisture content
$(C_6H_5COO)_2$
Reagent grade
Kishida Chemical Co., Ltd.

2,2′- azo-bis-isobutyronitrile (AIBN), MW = 162.22
$(CH_3)_2C(CN)N=NC(CN)(CH_3)_2$
Reagent grade
Kishida Chemical Co., Ltd.

2,2′-azo-bis-2,4-dimethylvaleronitrile (ADVN); V-65, MW = 248.0
$CH_3CH(CH_3)CH_2C(CN)(CH_3)N=NC(CN)(CH_3)(CH_2)CH(CH_3)CH_3$
Reagent grade
Wako Pure Chemical Industries Co., Ltd.

3.1.1.3 Hydrophobic additives/reagents

n-Hexadecane (n-Cetane), MW = 226.45
$CH_3(CH_2)_{14}CH_3$
Reagent grade
Tokyo Chemical Industry Co., Ltd.

1-Dodecanol (Lauryl alcohol), MW = 186.34

$CH_3(CH_2)_{10}CH_2OH$

Reagent grade

Kishida Chemical Co., Ltd.

1-Hexadecanol (Cetyl alcohol), MW = 242.45

$CH_3(CH_2)_4CH_2OH$

Reagent grade

Kishida Chemical Co., Ltd.

Palmitic Acid Methyl Ester (Methyl Palmitate), MW = 270.46

$CH_3(CH_2)_{14}COOCH_3$

Reagent grade

Tokyo Chemical Industry Co., Ltd.

Lauric Acid Methyl Ester (Methyl Laurate), MW = 214.35

$CH_3(CH_2)_{10}COOCH_3$

Reagent grade

Tokyo Chemical Industry Co., Ltd.

Bees wax; white

Commercial grade

3.1.1.4 Stabilizers

Poly(vinyl alcohol) (PVA); PVA-217 Degree of polymerization =1700, 88.5% saponification

Kurare Co., Ltd.

Sodium Dodecyl Sulfate; Sodium Lauryl Sulfate (SLS)

$CH_3(CH_2)_{11}OSO_3Na$

Biochemical grade

Merck Co., Ltd.

3.1.1.5 Solvents

Methyl alcohol, MW = 32.4

CH_3OH

Commercial grade

Kishida Chemical Co., Ltd.

3.1.1.6 Other chemicals

Sodium sulfate anhydrous, MW = 142.04

Na_2SO_4

Commercial grade

Kokusan Chemical works

Hydroquinone

$HO(C_6H_4)OH$

Reagent grade

Kishida Chemical Co., Ltd.

Sodium nitrite, MW = 69.0

$NaNO_2$

Reagent grade

Kishida Chemical Co., Ltd.

3.1.2 Apparatus

3.1.2.1 SPG emulsification apparatus

Microporous glass membrane (SPG membrane; trade name), an annulus cylinder diameter 10 mm, length 20 mm, pore sizes 0.9 and 1.42 μm

Oil tank capacity, 20 cm^3

Emulsion storage tank, 300 cm^3

SPG stainless steel module (SPG membrane inserted)

3.1.2.2 Polymerization

Three-necked glass separator flask, 300 cm^3	1 unit
Dimroth spiral condenser	1 unit
Nitrogen inlet-nozzle	1 unit
Nitrogen outlet tube	1 unit
Semicircular anchor-type blade	1 unit
Agitator	1 unit
Thermostat bath	1 unit
Nitrogen	1 unit

3.1.3 Analytical instruments

Optical microscope (OM); Olympus DP-10

Scanning Electron Microscope (SEM); JEOL JSM-5310

Gel Permeation Chromatography (GPC); Tosoh HLCH820

Nuclear Magnetic Resonance Spectroscope (NMR); JNM A500FT

Fourier-Transform Infrared Spectroscope (FT-IR); Nicolet

Differential Scanning Calorimeter (DSC); MAC SCIENCE 3100

3.2 Procedures

3.2.1 Purification of monomers

All commercial grade of monomers were purified prior to use. For DVB, EGDMA and 2-EHMA, the inhibitor was removed by washing the monomer with 5% aqueous NaOH. Roughly equal parts of the basic solution and the mixture are placed in a separator funnel and mixed with tumbling. The aqueous phase was drained off, the process was repeated three times. Then, the monomer was washed with distilled-deionized water five times. The drying agent, 4 Å was added in monomer and with mildly tumbling, drying overnight. The monomer was distilled under vacuum and keep in refrigerator prior used.

3.2.2 Emulsification

A schematic diagram of emulsification kit apparatus was shown in Figure 3.1. A microporous glass membrane was an annulus cylinder (10 mm outside diameter × 20 mm length) was installed in a pressure tight SPG module (stainless steel). Membrane pore sizes 0.9 and 1.42 μm were used. The model of the cross-section of membrane was shown in Figure 3.2. The dispersion phase, containing a mixture of monomers, hydrophobic additives and an initiator was stored in 20 cm^3 oil storage tank. Precisely controlled nitrogen pressure was applied to the oil storage tank of the dispersion phase. Three digit pressure gauge was used. The dispersion phase was allowed to permeate through microporous membrane, the module was completely immerse in an emulsion storage tank containing the continuous phase. The droplets were stabilized by the adsorption of PVA and cosurfactant SLS dissolved in the continuous phase which was stirred gently at 300 rpm with a magnetic bar to prevent the creaming of the droplets. After all an amount of dispersion phase was emulsified, the emulsion was transferred to the reactor and polymerized.

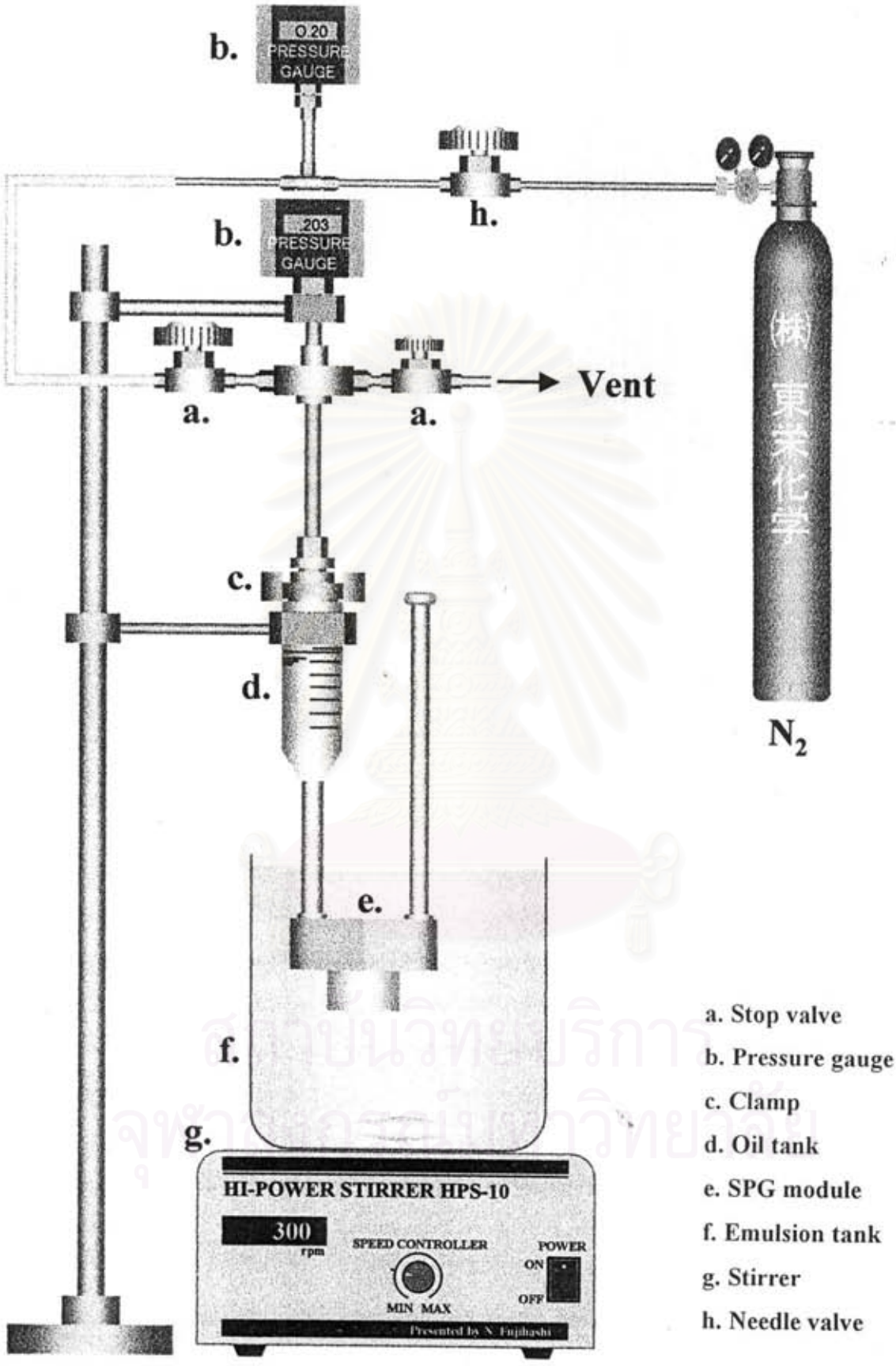

Figure 3.1 SPG emulsification kit

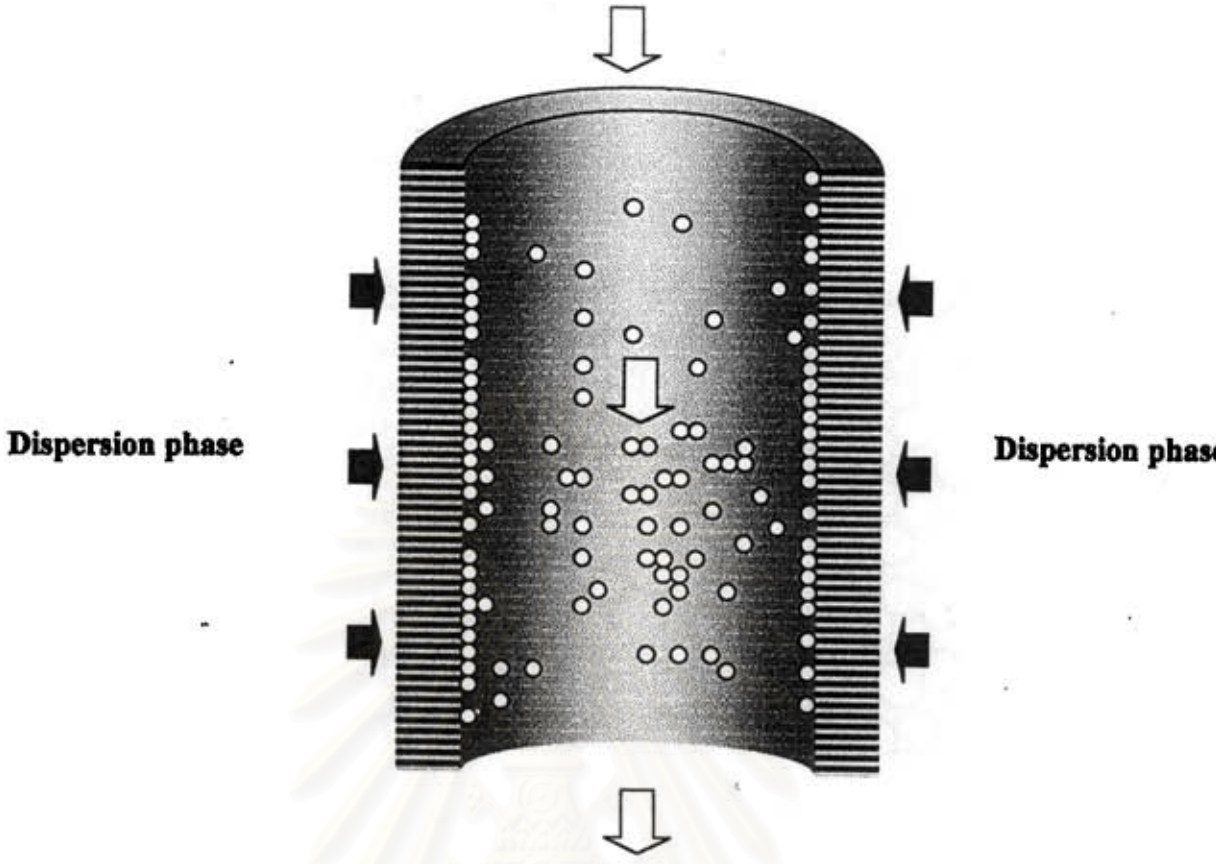

Figure 3.2 The cross- section model of SPG membrane

3.2.2.1 Preparative condition of copolymer by using the SPG pore size 1.42 μm

Dispersion phase was stored in 20 cm^3 oil storage tank. Nitrogen pressure in the range 0.30-0.45 Kgf/cm^2 was applied. The oil droplets were dispersed in the continuous phase containing PVA-217 as stabilizer in the concentration 6.50×10^{-3} g/cm^3 of water, SLS in the concentration 1.74×10^{-4} g/cm^3 of water, and Na_2SO_4 in the concentration 0.022 g/cm^3 of water, respectively. A photograph of emulsion droplets prepared with the SPG pore size 1.42 μm is shown in Figure 3.3a.

3.2.2.2 Preparative condition of copolymer by using the SPG pore size 0.90 μm

Dispersion phase was stored in 20 cm^3 oil storage tank. Nitrogen pressure in range 0.45-0.70 Kgf/cm^2 was applied. The oil droplets was dispersed in the continuous phase containing PVA-217 as stabilizer in the concentration 0.02 g/cm^3 of

water, SLS in the concentration 0.052 g/cm^3 of water, and Na_2SO_4 in the concentration 0.022 g/cm^3 of water, respectively. A photograph of emulsion droplets prepared with the SPG pore size 1.42 μm is shown in Figure 3.3b.

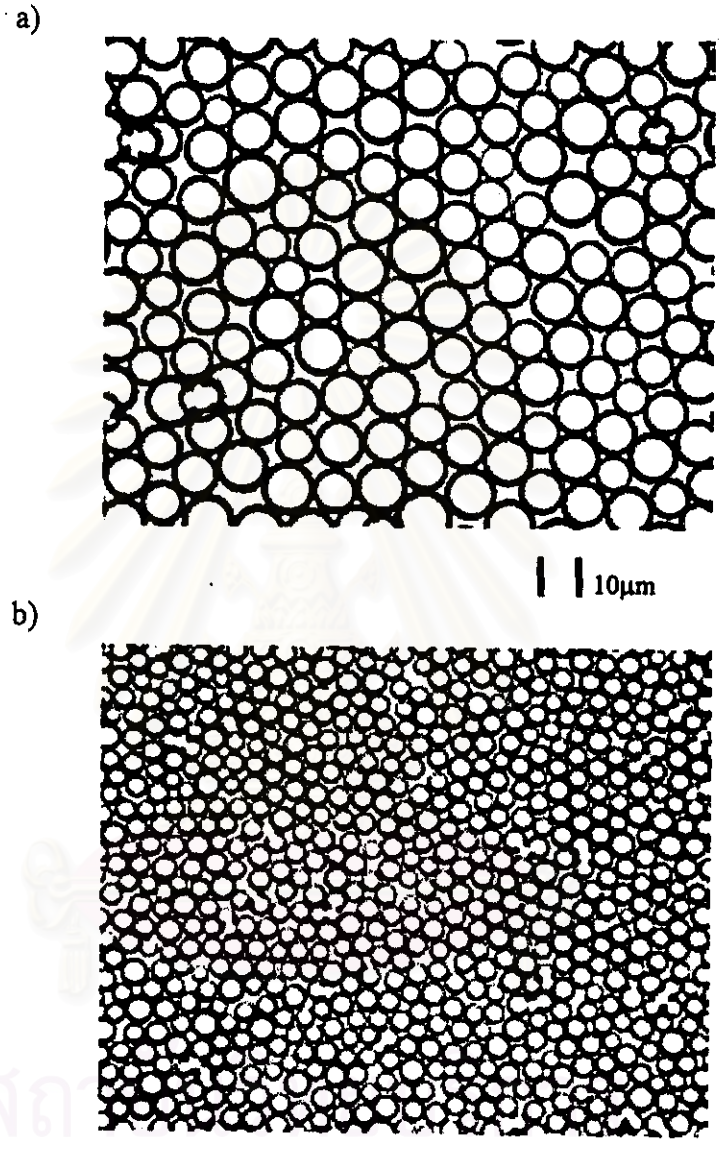

Figure 3.3 Photographs of emulsion droplets taken by an optical microscope: a) Using SPG pore size 1.42 μm, and b) SPG pore size 0.9 μm, respectively.

3.2.3 Polymerization

The obtained emulsion was transferred to a three-necked glass separator flask 300 cm^3 connected with a semicircular anchor-type blade for agitation, a spiral condenser, and a nitrogen inlet nozzle. Gently N_2 gas was bubbled into the emulsion for 1 h, the nozzle was lifted above the emulsion level and the temperature was increased to 75°C and polymerized for 24 h under a nitrogen atmosphere. The reactor was shown in Figure 3.4.

3.2.4 Treatment of polymer particles

After the polymerization, polymer particles were removed from the latex by centrifugation at 3000 rpm, washed repeatedly with methyl alcohol and dried under vacuum at room temperature for 24 h.

3.3 Characterization

3.3.1 Percent conversion of monomer

Percent conversion of the monomer was determined by gravimetric method. After the polymerization, 5 cm^3 of the polymer latex was collected in 20 cm^3 weighing bottles, 10-15 cm^3 of methyl alcohol was added to precipitate the polymer. Polymer particles were separated by centrifugation at 3000 rpm, washed repeatedly with methyl alcohol 2-3 times. The polymer particles were dried in vacuum at room temperature and the weight was measured.

3.3.2 Monomer droplets diameter

Monomer droplets before polymerization and polymer particles were observed with an optical microscope. Diameters of droplets about 200 droplets were measured to calculate an average diameter and a size distribution.

3.3.3 Polymer particles diameter

The external morphology of polymer particles was determined by JEOL model JSM-5310 scanning microscope. In scanning electron microscopy (SEM), the specimens were prepared by dilution of polymer latex, diluted latex was dropped on an aluminium stub surface. The specimens were coated with a thin layer of gold (about 60 Å in thickness) under reduced pressure (below 10^{-2} Pa) using a fine coater JEOL model JFC-1200. On an average, the diameters of 200 polymer particles in its actual size from SEM images were counted. In some cases, the diameters of large-sized polymer particles were counted from the optical microscope image.

The average droplet size (D_e) and polymer particle diameter (D_p), standard deviation (σ), and a coefficient of variation (CV) were calculated using the formulas:

$$D_n = \left(\frac{\sum_{i=1}^{n} n_i D_i}{\sum_{i=1}^{n} n_i} \right) \qquad (3.1)$$

Where n_i is the number of particle diameters, D_i and D_n correspond to the exact mean of the population. The standard deviation, σ, is determined from the measured particle diameters as the following.

$$\sigma = \left[\frac{1}{N-1} \sum_{i=1}^{N} (D_i - \overline{D})^2 \right]^{1/2} \qquad (3.2)$$

The particle size distribution is reflected in the standard deviation. The breadth of the particle size distribution was defined as being proportional to the standard deviation of the particle diameters using the coefficient of variation as follows:

$$\text{Coefficient of variation (CV)} = \sigma / D_n \qquad (3.3)$$

3.3.4 Average molecular weight and molecular weight distribution (GPC)

The GPC chromatograms were obtained by using Tosoh gel permeation chromatography model HLCH820. Chromato column at the oven temperature 40°C and the injection temperature at 35°C in a range 64. Pressure was applied to sample at 16 kg/cm^{2}G and reference at 12 kg/cm^{2}G. The two types of GPC columns for sample analysis, the first column model GRCX4 and the second column model GMMXL were packed with mixed gels of poly(divinylbenzene-co-styrene), respectively. The reference column model GMMXL was packed with mixed gels of poly(divinylbenzene-co-styrene). Tetrahydrofuran (THF) was used as solvent and carrier.

For analytical by preparative process, 1 mg of dried polymer sample was dissolved into 2 cm^3 of THF, an approximate concentration was 0.1 wt%. Then, the polymer solution was injected into the column at a flow rate 0.5 cm^3/min.

3.3.5 Glass transition of polymer

Measurements of glass transition temperature (Tg) were made by using a MAC Science model 3100 differential scanning calorimeter. 50-80 mg of the sample was placed in the aluminium pan and was put on the sensor at room temperature along with an empty pan as a reference to assist output balance. Measurement of the sample was done at a heating rate 10°C per minute. For a random copolymer, the Tg is given by Fox equation.

$$\frac{1}{Tg_{12}} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2} \qquad (3.4)$$

where W_1 and W_2 are the weight fractions of monomer 1 and 2, and Tg_1 and Tg_2 are the transition temperatures of homopolymer (see Appendix B)

3.3.6 Functional group of copolymer

The FT-IR, Nicolet Fourier Transform Infrared Spectrometer was used for characterizing the functional groups of the copolymer. Polymer samples were prepared by KBR pellet method.

3.3.7 Copolymer Composition

The copolymer composition was calculated from the structural components as a chemical shift, commonly measured in ppm from an internal reference. The polymer can provide information on number and type of atoms linked to each particular nucleus. Proton NMR spectra (^{1}H NMR) are complicated by the presence of coupling effects between the spins of the protons. ^{1}H NMR spectra were recorded with 500 MHz with JNM-A500 FT spectrometer at 318 K, by using deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as internal reference. The sample concentration was 30% w/v $CDCl_3$. A total of 160 scans was accumulated, corresponding to a spectral width 10000 Hz, an acquisition time of 3.2768 s, and a pulse delay of 3.7232 s. Monomer composition in copolymer was determined by comparing relative peak areas of proton.

The copolymer composition of poly(styrene-co-methyl methacrylate); St-MMA was calculated by using the peak area of $-C_6\underline{H}_5$ (styrene) at the chemical shift (δ) from 6.3 to 7.6 ppm and the peak area of $-C\underline{H}_3$ (MMA) at the δ from 0.1-1.1 ppm. The follow equation was used to calculate the content of styrene:

$$\text{Styrene (wt\% in copolymer)} = \frac{A(-C_6\underline{H}_5)/5}{A(-C_6\underline{H}_5)/5 + A(-C\underline{H}_3)/3} \qquad (3.5)$$

where A represents the peak area of proton.

The copolymer composition of poly(styrene-co-n-butyl methacrylate); St-n-BMA and poly(styrene-co-2-ethylhexyl methacrylate); St-2-EHMA were calculated by using the peak areas of $-C_6\underline{H}_5$ (styrene) at the chemical shift(δ) from 6.3 to 7.6 ppm and the peak area of $-C\underline{H}_3$ (n-BMA or 2-EHMA) at δ from 0.1-1.1 ppm. The calculation also followed eq. 3.5

The terpolymer composition of poly(styrene-co-methyl methacrylate-co-n-butyl methacrylate); St-MMA-n-BMA were calculated by using the peak area of $-C_6\underline{H}_5$ (styrene) at the chemical shift(δ) from 6.3 to 7.6 ppm, peak area of $-C\underline{H}_3$ (MMA+n-BMA; main chain) and $-C\underline{H}_2-C\underline{H}_2-$ (n-BMA; side chain) at the δ from 1.1 to 2.6 ppm, and the peak area of $-C\underline{H}_3$ (n-BMA) at the δ from 0.1-1.1 ppm. The following equation was used to calculate the content of styrene:

Styrene (wt% in terpolymer)

$$= \frac{A(-C_6\underline{H}_5)/5}{A(-C_6\underline{H}_5)/5 + A\left[(-C\underline{H}_3)_{(n\text{-BMA+MMA})} + (-C\underline{H}_2C\underline{H}_2-)_{(n\text{-BMA})}\right]/7 + A(-C\underline{H}_3)/3} \quad (3.6)$$

The terpolymer composition of poly(styrene-co-methyl methacrylate-co-2-ethylhexyl methacrylate); St-MMA-2-EHMA were calculated using the peak area of $-C_6\underline{H}_5$ (styrene) at the chemical shift (δ) from 6.3 to 7.6 ppm, the peak area of $-C\underline{H}_3$ (MMA+2-EHMA; main chain) at the δ from 0.36 to 1.36 ppm, and peak area of $-(C\underline{H}_2)_3C\underline{H}C\underline{H}_2-$ (2-EHMA; side chain) and $CH_3-(C\underline{H}_2)_3-$ (2-EHMA)); side chain) at the δ from 0.36-1.36 ppm. The follow equation was used to calculate content of styrene:

Styrene (wt% in terpolymer)

$$= \frac{A(-C_6\underline{H}_5)/5}{A(-C_6\underline{H}_5)/5 + A\left[((-C\underline{H}_2)_3C\underline{H}C\underline{H}_2-)_{(2\text{-EHMA})} + (-C\underline{H}_3)_{(MMA)}\right]/12 + A(CH_3(C\underline{H}_2)_3-)/6} \quad (3.7)$$

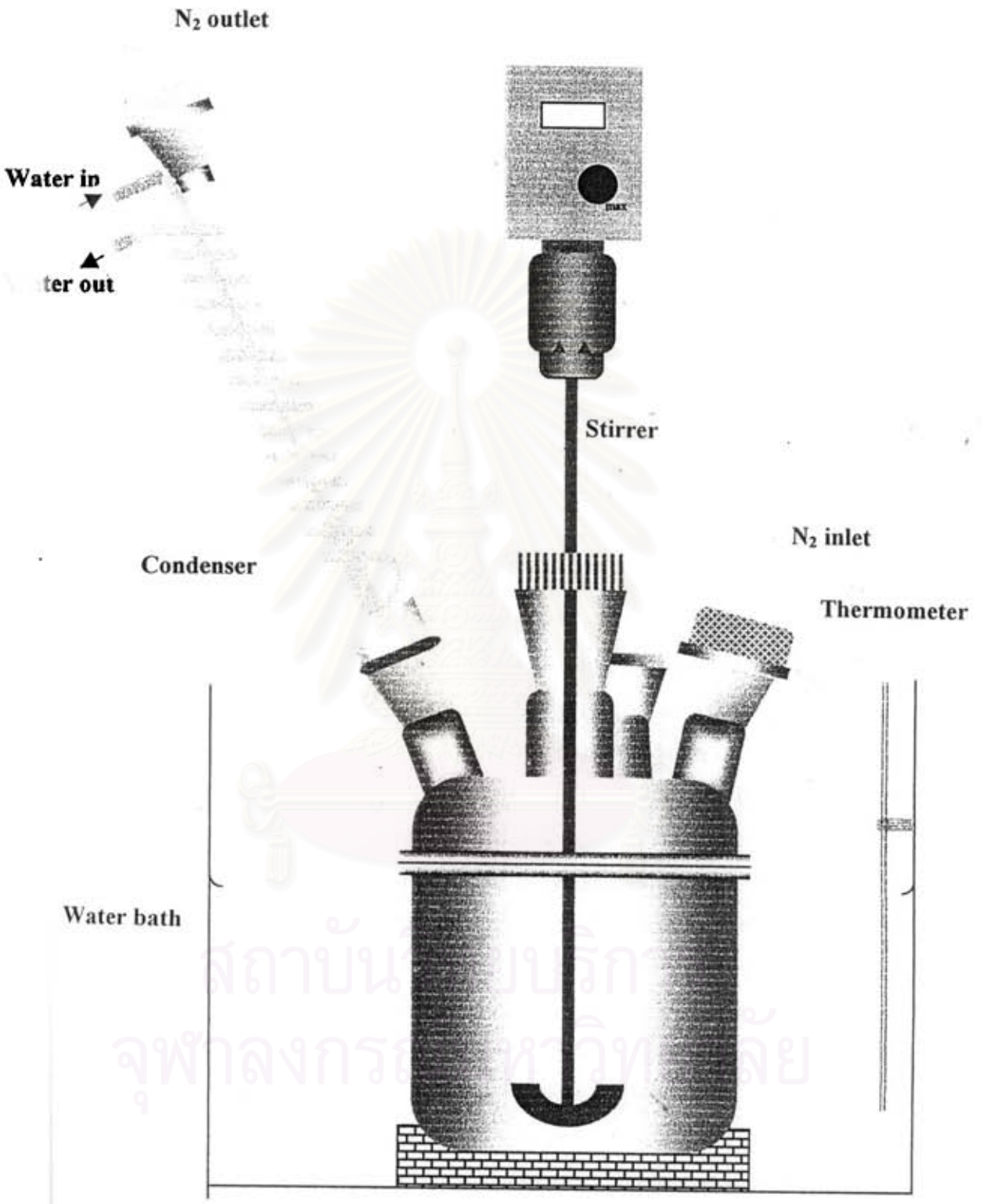

Figure 3.4 Suspension polymerization reactor